

Enthalpy

When a chemical reaction takes place these two processes occur and there is often an exchange of heat energy between the reaction and its surroundings.

This is called the enthalpy change (ΔH).

Every substance has an enthalpy (a chemical potential energy or heat content) that cannot be measured. Only when substances react can the enthalpy **change** be measured.

In order that chemists worldwide can compare results of thermochemical experiments, a series of special conditions have been agreed.

Enthalpy changes are defined as the **measured** heat energy changes occurring during a reaction, usually per mole of product formed or reactant used up, depending on the particular enthalpy change being defined. The units are in kilojoules per mole, (kJ mol^{-1}).

The **standard** enthalpy change is defined as the enthalpy change **measured under standard conditions**.

Standard conditions are one mole of a substance at one atmosphere pressure and any specified temperature (in Kelvin).

The symbol used is ΔH° .

The temperature specified is usually 298 K (25°C) and ΔH° is taken to mean ΔH° at this temperature.

Enthalpy of formation

The standard enthalpy of formation (ΔH°_f) of a compound is defined as the enthalpy change when one mole of a compound is formed from its elements in their **standard** states.

The standard enthalpy of formation of elements is by definition zero (because this is the way they are found), giving a base line from which enthalpy changes can be measured.

The standard enthalpy of combustion (ΔH°_c) of a substance is the enthalpy change (always energy released) when one mole of a substance is completely burned in excess oxygen.

An excess of oxygen has to be used to ensure complete oxidation, e.g. for carbon to ensure that CO_2 is the only product and no CO is formed.

The enthalpy change for any reaction is defined as the sum of the enthalpy of the products minus the sum of the enthalpy of the reactants:

$$\Delta H = \sum \text{enthalpy of products} - \sum \text{enthalpy of reactants}$$

Σ = the sum of

This means that exothermic reactions have a negative ΔH value as energy is lost to the surroundings, while endothermic processes have a positive ΔH value as energy is taken in by the reaction from the surroundings.

Hess's law

The first law of thermodynamics simply states that "energy cannot be created or destroyed and can only be changed from one form to another"

Hess, in 1840, applied this law to chemical reactions and Hess's law states that 'the enthalpy change associated with converting reactants in a specified state into products in a specified state is independent of the route taken' (you already know this from Higher)

e.g. for the oxidation of carbon:

- (a) $\text{C(s)} + \text{O}_2\text{(g)} \rightarrow \text{CO}_2\text{(g)}$ $\Delta H_a = -394 \text{ kJ mol}^{-1}$
 (b) $\text{C(s)} + \frac{1}{2}\text{O}_2\text{(g)} \rightarrow \text{CO(g)}$ $\Delta H_b = -123 \text{ kJ mol}^{-1}$
 (c) $\text{CO(g)} + \frac{1}{2}\text{O}_2\text{(g)} \rightarrow \text{CO}_2\text{(g)}$ $\Delta H_c = -271 \text{ kJ mol}^{-1}$
 Equation (a) is the sum of equations (b) and (c)

Equations can be rearranged in order to calculate an unknown value of ΔH . This has already been covered at Higher.

There are essentially two methods of calculating ΔH by applying Hess's Law, the mathematical method and the pictorial method.

The mathematical method requires writing equations and multiplying them by appropriate numbers and reversing them where necessary so that the overall equation is equal to the sum of the other equations. The pictorial method involves drawing a thermochemical cycle (at Higher this may have been called a Hess's Law triangle), and putting ΔH values to each step.

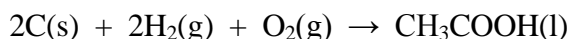
Each method is equally valid and will produce the same result.

Some students prefer the mathematical method while others are better at seeing figures on a diagram and will use the pictorial method. Make sure you use the method that you feel most comfortable with.

Worked example – ΔH from heats of combustion

Calculate the standard enthalpy of formation of ethanoic acid given that its standard enthalpy of combustion is -876 kJ mol^{-1} and that the standard enthalpies of formation of carbon dioxide and water are -394 and -286 kJ mol^{-1} .

Step 1 write down the required equation



Step 2 write down the equations for the formation of carbon dioxide and water, and for the combustion of ethanoic acid.

- (1) $\text{C(s)} + \text{O}_2\text{(g)} \rightarrow \text{CO}_2\text{(g)}$ $\Delta H = -394 \text{ kJ}$
 (2) $\text{H}_2\text{(g)} + \frac{1}{2}\text{O}_2\text{(g)} \rightarrow \text{H}_2\text{O(l)}$ $\Delta H = -286 \text{ kJ}$
 (3) $\text{CH}_3\text{COOH(l)} + 2\text{O}_2\text{(g)} \rightarrow 2\text{CO}_2\text{(g)} + 2\text{H}_2\text{O(l)}$ $\Delta H = -876 \text{ kJ}$

To obtain the equation of formation, equation (1) must be multiplied by 2, equation (2) must be multiplied by 2 and equation (3) must be reversed, and the ΔH values must also be changed.

- (1) $2\text{C(s)} + 2\text{O}_2\text{(g)} \rightarrow 2\text{CO}_2\text{(g)}$ $\Delta H = -788 \text{ kJ}$
 (2) $2\text{H}_2\text{(g)} + \text{O}_2\text{(g)} \rightarrow 2\text{H}_2\text{O(l)}$ $\Delta H = -572 \text{ kJ}$
 (3) $2\text{CO}_2\text{(g)} + 2\text{H}_2\text{O(l)} \rightarrow \text{CH}_3\text{COOH(l)} + 2\text{O}_2\text{(g)}$ $\Delta H = +876 \text{ kJ}$

If these equations are now added together and the substances appearing on both sides are removed by cancelling, we obtain the overall equation. It is now simply a case of adding the ΔH values.

$$\Delta H = 876 + (-572) + (-788) = -484 \text{ kJ}$$

Therefore, the standard enthalpy of formation of ethanoic acid is -484 kJ mol^{-1} .

Note that this does not mean that this reaction actually happens. There is no magic reaction vessel which gets supplied with black carbon powder and hydrogen and oxygen gases at one end, and turns

out ethanoic acid at the other, but if there were, each mole of acid produced would also produce 484 kJ of heat energy.

This value is useful in calculations for reactions producing ethanoic acid by other methods such as the oxidation of ethanol. When designing a chemical plant, chemical engineers need to know how much heat is produced or how much must be supplied if the reaction is endothermic.

Practice example

The Monsanto process for the production of ethanoic acid involves directly combining methanol and carbon monoxide (the carbonylation of methanol).

- 1) write an equation for this reaction
- 2) write the equations for the combustion of methanol, carbon monoxide and ethanoic acid
- 3) given the heats of combustion of methanol, carbon monoxide and ethanoic acid are -727, -271 and -876 kJ mol⁻¹ respectively, calculate ΔH for this process.

Worked example – ΔH from heats of formation

Calculate the standard enthalpy of reaction for the decomposition of copper(II) nitrate from the given standard enthalpies of formation.

Equation



Enthalpies of formation:

Copper (II) nitrate	-307
Copper (II) oxide	-155
Nitrogen dioxide	+34
Oxygen	0

From the equation that $\Delta H = \sum$ enthalpies of products - \sum enthalpies of reactants, the calculation is

$$\begin{aligned} & (-155) + (2 \times +34) + 0 - (-307) \\ & = -155 + 68 + 0 + 307 \\ & = +220 \text{ kJ, so the reaction is quite endothermic.} \end{aligned}$$

This method is obviously more convenient to use than the method required for enthalpies of combustion, but you must have data on this and must always take the heat of formation of an element in its natural state to be zero.

Reaction feasibility

The word “feasible” means “likely to happen”. Make sure you understand this meaning.

Chemical reactions can be used to provide energy to do work. In the engine of a car and in a rocket engine, chemicals are burned and their energy is converted into work.

One basic fact of thermodynamics is that the conversion of energy into work is never 100% efficient (a petrol engine is around 25% efficient) and the work energy derived from a chemical reaction is always less than the heat energy (ΔH) that is used. A small part of the heat change is never converted into work and is referred to as “unavailable” energy.

It is therefore possible to write the equation

$$\Delta H = \text{work energy} + \text{'unavailable' energy}$$

In thermodynamic terms this is changed into:

$$\Delta H = \text{free energy} + \text{entropy energy}$$

These two terms are explained in the following sections.

Entropy

In nature there is a tendency towards disorder.

A brick wall changes into a disordered heap of bricks either with age or the demolition squad, but the reverse process does not take place spontaneously, i.e. without outside help.

More widely, an untended garden, diffusion, corrosion and the dispersion of sewage into the sea are all examples of systems naturally tending towards disorder.

In thermodynamic terms disorder is called entropy.

The degree of disorder in a system is called the entropy of that system. The greater the disorder, the greater the entropy.

The molecular motion of any substance depends on its state. Solids only have vibrational motion while gases have vibration, rotation and linear motion.

It therefore follows that entropy increases as temperature increases and that changes in state, such as melting and evaporation, involve large changes in entropy.

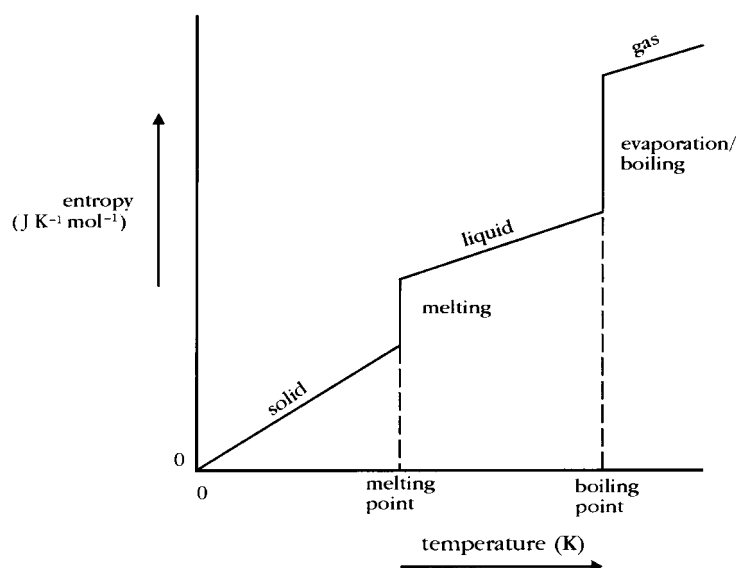
When a state change occurs there is a change in entropy without a change in temperature and this is linked to the concept of latent heat.

For the non-physicists, any substance changing state involves an energy change without a temperature change. To turn 1 kg of water at 100°C into 1 kg of steam at 100°C requires 2257 kJ of energy. This is known as latent (hidden) heat, and the example shown, is known as the latent heat of evaporation of water. It can be thought of as the energy required to break any forces between molecules to completely separate them. In the case of water, fairly strong hydrogen bonds must be broken, so water has a high latent heat of evaporation.

There are many sources of information on latent heat. One is

http://www.engineeringtoolbox.com/fluids-evaporation-latent-heat-d_147.html

The relationship between disorder (entropy) and temperature is shown:



This diagram relates to no specific substance, but pay close attention to the units on the graph.

- The temperature is always in Kelvin. As previously learned, temperature is a measure of how much energy (kinetic, vibrational etc.) that particles possess. At absolute zero, particles have stopped moving completely and therefore possess no energy.
- As entropy is related to temperature, the units must take account of this. Entropy values for a substance are measured in **Joules per mole per Kelvin unit, or $\text{J mol}^{-1} \text{K}^{-1}$** .
- You are already very familiar with enthalpy being measured in kilojoules per mole. It is very easy to get “caught out” when doing calculations involving both enthalpy (in kJ) and entropy (in J). Be careful of this.

At absolute zero (0 K) a crystal lattice has perfect order and therefore zero entropy. This is one version of the **third law of thermodynamics**.

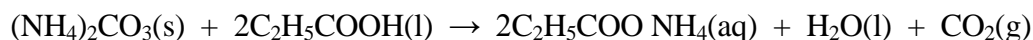
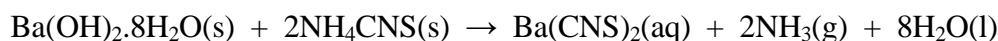
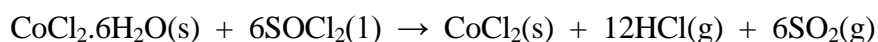
As the solid is heated its particles gain more kinetic energy and the entropy increases slowly. There is a rapid increase in entropy at the melting point and boiling point, with a greater increase at the boiling point than at the melting point. In other words, the entropy of a system is temperature dependent.

The **second law of thermodynamics** states that the total entropy of a reaction system and its surroundings **always increases** for a **spontaneous process**. A spontaneous process is a process that is thermodynamically possible and this means that it can take place on its own irrespective of how long this requires.

The second law of thermodynamics can go much of the way to explaining why endothermic reactions actually happen. As you already know, in an endothermic reaction, the products have more energy than the reactants. This is not likely to happen as reactions would take place to bring about a decrease in energy, not an increase.

If the creation of disorder (increase in entropy) is also factored in, then endothermic reactions are likely to be feasible.

Consider the following endothermic reactions



It is clear that the entropy of the system increases just by looking at the changes in state from reactants to products. They all produce a gas where there was no gas before, and gases have much higher entropy values than solids or liquids.

Entropy values for common elements and compounds are listed on page 16 of the Data Book. Notice the large difference in values between liquids and gases.

In the examples above, the entropy increase is so large that it more than overcomes the unfavourable enthalpy changes and the reactions are spontaneous.

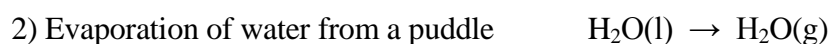
We can see that the second law requires that both system and surroundings be taken into account. Heat energy released by a reaction into the surroundings increases the entropy of the surroundings (exothermic reactions heat up the surrounding air, making it more disordered) while heat absorbed by a reaction system from the surroundings decreases the entropy of the surroundings.

The change in entropy of the surroundings that occurs as a result of such a reaction can be calculated from the temperature and entropy change during the reaction.

Consider the following reactions or changes



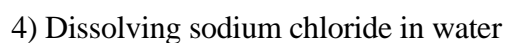
This reaction has a decrease in entropy. Gaseous oxygen molecules become part of the ionic compound MgO. The reaction is highly exothermic however and the heat energy given off causes an overall increase in entropy.



This is a process rather than a reaction, however the laws of thermodynamics still apply. The process is endothermic but the change from liquid to gas means a large increase in entropy, so the entropy of the system plus surroundings increases.



This reaction has a large decrease in entropy - gas molecules becoming a solid. The reaction is quite exothermic however, and the heat released causes an increase in the entropy of the surroundings, so the entropy of the system plus surroundings increases.



This process has an enthalpy value of almost zero, so no change to the entropy of the surroundings. An ionic crystal breaks up to become ions evenly spread through the water, so the entropy of the system increases.

Standard entropy

Entropy has the symbol S.

Standard entropy is the entropy of a substance measured under standard conditions. You have met this idea before. Standard conditions are:

- 1 mole of substance
- 1 atmosphere pressure for gases
- 1 mole per litre for solutions
- 298K (25°C)

When these conditions are met, the symbol becomes S^0 .

Entropy change

When a reactant changes into a product, the entropy associated with the reactant “disappears” and is replaced with the entropy associated with the product. The change in entropy, ΔS , can be easily calculated by the equation:

$$\Delta S = \sum \text{entropy of products} - \sum \text{entropy of reactants}$$

you have met this type of equation already when calculating enthalpy changes.

The equation linking enthalpy, entropy and feasibility.

Statements such as “the entropy change overcomes the unfavourable enthalpy change” can help you to understand why a reaction or process takes place, but to be truly scientific, the statement has to be quantified, and this means applying an equation.

From page 1, a simple thermodynamic equation was established

$$\Delta H = \text{free energy} + \text{entropy energy (where entropy was the energy “unavailable” to do work)}$$

rearranging, free energy = ΔH - entropy energy

adding in the temperature factor since entropy is temperature dependent

$$\text{free energy} = \Delta H - (\text{entropy energy} \times \text{temperature})$$

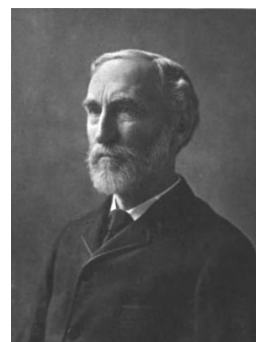
$$\text{free energy} = \Delta H - T\Delta S \text{ (where T is measured in Kelvin units)}$$

finally, assigning a symbol to free energy. The symbol used is G after Josiah Willard Gibbs

http://en.wikipedia.org/wiki/Josiah_Willard_Gibbs

$$\Delta G = \Delta H - T\Delta S$$

This is the equation which governs whether or not a chemical reaction is feasible. A reaction will only be feasible if ΔG is negative. ΔH and ΔS can be either positive or negative, but when combined in the equation must produce a negative value for ΔG .



If the enthalpy and entropy changes for a reaction are known, it is possible to determine the feasibility of a reaction at any temperature.

If measurements are made under standard conditions, the equation becomes

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

*It's fair to say that many reactions are **not** carried out under standard conditions. The reduction of iron ore with carbon monoxide in a blast furnace is an obvious example of this, but where possible, standard conditions are met.*

Note also that this equation does not predict anything about reaction rate. Some reactions have a high activation energy to overcome and therefore will not start unless energy is supplied initially, but once started will keep going.

One important use of the equation is to determine if there is a temperature at which a reaction becomes feasible.

Consider the production of lime (calcium oxide) from limestone (calcium carbonate)

Equation:	$\text{CaCO}_3(\text{s}) \rightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$			
Heats of formation	-1208	-635	-394	kJ mol^{-1}
Entropy values	93	40	214	$\text{J mol}^{-1} \text{K}^{-1}$

The substance will not decompose at room temp (25°C). Prove this by using Gibbs' equation

1) Calculate ΔH

$$\begin{aligned}\Delta H &= \sum \Delta H \text{ of products} - \sum \Delta H \text{ of reactants} \\ &= -635 + (-394) - (-1208) \\ &= 1208 - 635 - 394 = +179 \text{ kJ mol}^{-1}\end{aligned}$$

2) Calculate ΔS (you may immediately spot that it is positive since a gas is formed)

$$\begin{aligned}\Delta S &= \sum S \text{ of products} - \sum S \text{ of reactants} \\ &= 40 + 214 - 93 = +161 \text{ J mol}^{-1} \text{K}^{-1} = 0.161 \text{ kJ mol}^{-1} \text{K}^{-1}\end{aligned}$$

again, be careful of units

3) Apply the equation with $T = 298\text{K}$

$$\begin{aligned}\Delta G &= \Delta H - T\Delta S \\ &= +179 - (298 \times 0.161) \\ &= 179 - 47.98 = +131.02 \text{ kJ mol}^{-1}\end{aligned}$$

ΔG is large and positive. The reaction is not feasible at room temp.

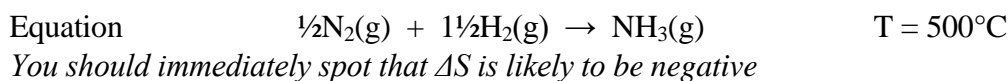
Is there a temperature at which it will be feasible?

To find this out, rearrange the equation to solve for T with $\Delta G = 0$

$$\begin{aligned}\Delta G &= \Delta H - T\Delta S \\ 0 &= +179 - (0.161T) & 0.161T &= 179 \\ T &= 179 \div 0.161 & &= 1111.8\text{K} = 838.8^\circ\text{C}\end{aligned}$$

ΔG and reversible reactions

Calculation of ΔG for the Haber process producing ammonia



Heats of formation 0 0 -46 kJ mol⁻¹

Entropy values 191.6 130.7 192.5 J mol⁻¹ K⁻¹

$$\begin{aligned}\Delta H &= \sum \Delta H \text{ of products} - \sum \Delta H \text{ of reactants} \\ &= -46 - 0 - 0 = -46 \text{ kJ}\end{aligned}$$

$$\begin{aligned}\Delta S &= \sum S \text{ of products} - \sum S \text{ of reactants} \\ &= 192.5 - (\frac{1}{2} \times 191.6) - (\frac{1}{2} \times 130.7) \\ &= 192.5 - 95.8 - 196.05 = -99.35 \text{ J mol}^{-1} \text{ K}^{-1} = 0.09935 \text{ kJ mol}^{-1} \text{ K}^{-1}\end{aligned}$$

$$\begin{aligned}\Delta G &= \Delta H - T\Delta S \\ &= -46 - (-0.09935 \times 773) \\ &= -46 + 76.8 = +30.8 \text{ kJ mol}^{-1}\end{aligned}$$

The calculation tells us that the reaction is not feasible, but millions of tonnes of ammonia are produced each year by this process. How?

The answer to this apparent contradiction lies in the fact that the reaction is reversible.

The reaction has a positive ΔG value **only if it goes 100% to completion.**

In fact, the reaction only goes a few % to completion i.e. the equilibrium lies to the left.

The fact that it proceeds to equilibrium tells us that ΔG is negative to this point.

To go further, ΔG would be positive, and, most crucially, to go back also means that ΔG is positive.

For any reversible reaction, ΔG is negative as it proceeds to equilibrium (from either side)

The position of equilibrium for any reaction depends on the equilibrium constant (K) which has already been covered.

There is a relationship between ΔG and K, but you do not need to know it for Advanced Higher. All you do need to know is that a reaction will proceed to the point of lowest free energy.

In the Haber process, ammonia is continually removed from the reaction mixture by cooling. The ammonia condenses (look at the boiling points of the three gases) and unreacted nitrogen and hydrogen are returned to the reaction vessel.

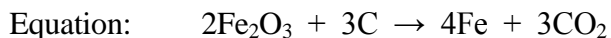
Note that thermodynamics cannot give any information about a reaction pathway or mechanism nor can it give any information about how fast a reaction is likely to proceed.

If a reaction is heated to the point where it just becomes feasible, it is likely to proceed very slowly, so it would be heated to a temperature considerably higher than this. In the example above, if limestone were heated to 839 or 840°C, it would proceed far too slowly to produce any decent quantity of lime.

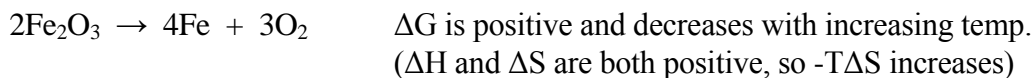
Ellingham diagrams

This is probably the most intellectually demanding part of thermodynamics.

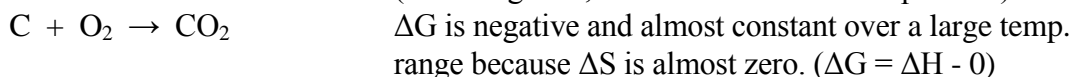
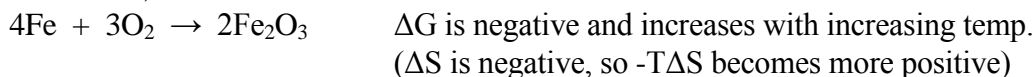
Consider the reduction of iron (III) oxide with carbon



This can be broken into 2 parts

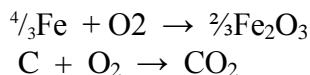


If this reaction is reversed, it becomes

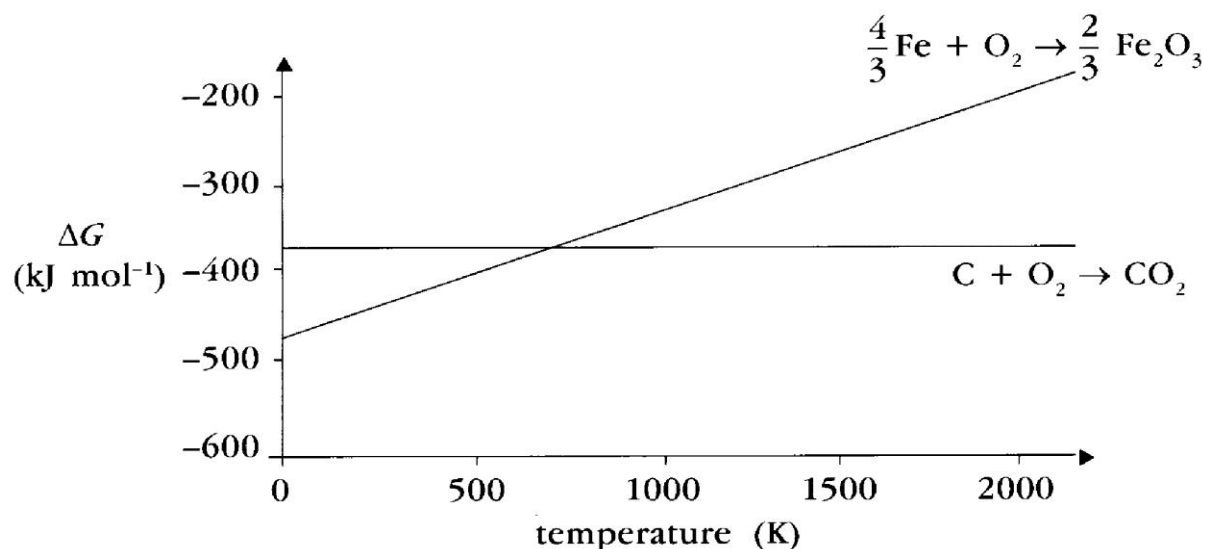


Before plotting a graph of ΔG against temperature, we must “standardise” each equation. This is done by making ΔG related to 1 mole of the element common to both equations, in this case oxygen.

The equations now become



If a graph of ΔG against temp is plotted for both reactions, we would get:



At low temperatures, The reaction of iron \rightarrow iron oxide is more feasible than carbon \rightarrow carbon dioxide (more negative ΔG), so carbon will not reduce iron oxide.

At the point where the lines cross, (about 700K), the ΔG values are equal. This is the point where the overall reaction starts to become feasible.

At temperatures greater than 700K, the reaction of carbon \rightarrow carbon dioxide has the more negative ΔG value, so the overall reduction reaction is feasible and iron is produced.

An important point to note is that a reduction will be feasible if the line of the reducing agent (carbon in this diagram) is **below** the line of the oxide being reduced.

Ellingham diagrams can be used to plan the reaction conditions required for metal extraction from ores. There are three general methods for the extraction of metals from their ores:

- reduction by a non-metal (usually carbon) or carbon monoxide produced from carbon.
- reduction by another (more reactive) metal
- electrolytic reduction.

The method adopted for each metal depends on relative costs. All three methods are possible for many metals, but the temperatures required for the first two methods may be impracticable. Only a general appreciation of the relative costs can be attempted since accurate information can be difficult to obtain, and is quickly out of date.

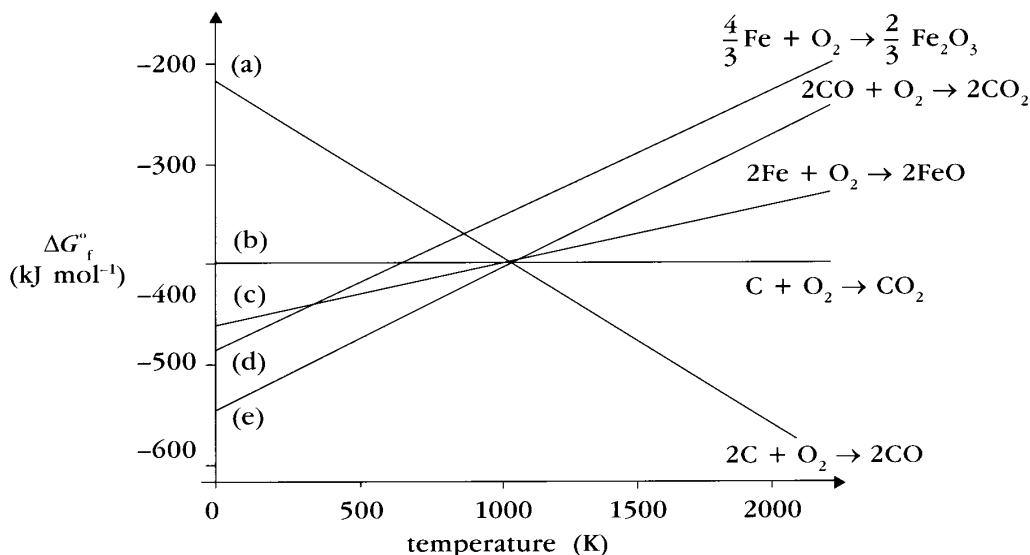
There are many factors that affect costs:

- Carbon is a cheap raw material
- The use of high temperatures is expensive, both because of the fuels required and the equipment required to withstand the temperature
- The use of high temperatures requires longer cooling times before furnaces can be tapped and consequently slows down the process
- Electricity for electrolytic reduction is expensive, but this may be the only practical method. Aluminium and the most reactive metals are extracted by electrolysis of their molten compounds.
- reduction by another metal necessarily makes the metal obtained more expensive than that consumed, but there may be no alternative method. Titanium can be obtained from its oxide by reduction with carbon, but the titanium metal formed will immediately react with carbon to form titanium carbide. Titanium is converted into its chloride and then this is reduced to the metal with magnesium. The magnesium chloride formed is recovered by electrolysis.

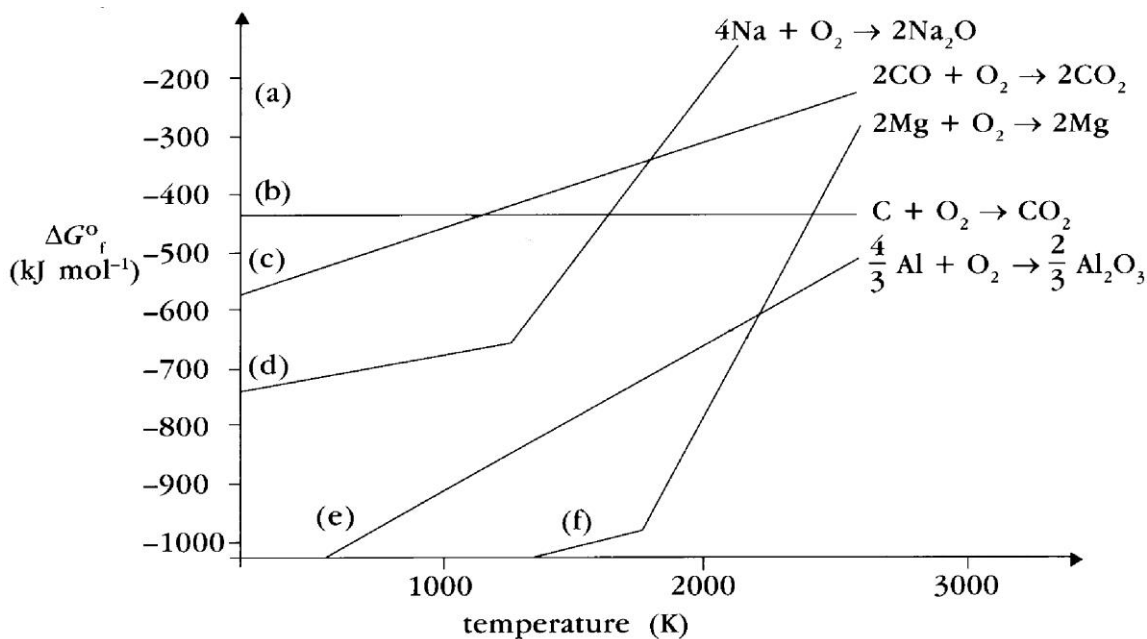
Reactions involving two solids (solid-solid reactions) are generally much slower than reactions involving a solid and a gas. From Int 2, you will know that the reduction of iron oxide in the blast furnace is done with carbon monoxide, not carbon.

From this general information, it is clear that non-metal reduction is much the cheapest method as long as the required temperature is not too high. A very high temperature causes chemical as well as economic problems: most metals form carbides at high temperatures, furnace linings may react with the metal being made, the reaction to produce the metal is reversible and cooling must be carried out under controlled conditions to prevent the reverse reaction.

The conditions for the extraction of iron in a blast furnace can be predicted from an Ellingham diagram of all the possible reactions. Two iron reactions are shown because some iron ores contain a mixture of iron (II) and iron (III) oxides. Notice each reaction contains 1 mole of oxygen.



The conditions for extraction of aluminium from its oxide (bauxite) can also be deduced from an Ellingham diagram.



It can be seen from the diagram that aluminium oxide cannot be reduced with carbon at temperatures lower than about 2800K (about 2500°C). Such temperatures are not obtainable as the walls of the furnace would probably melt.

Aluminium can be reduced at temperatures **below** about 2300K with magnesium (lines (e) and (f)) but the high cost of magnesium makes the electrolytic process more economical.

Remember - the line of the reducing agent must be below the line of the oxide being reduced.

It is interesting to note that aluminium cannot be obtained from its oxide by reacting with sodium.

The reaction is never thermodynamically feasible. Aluminium was first obtained from its compounds by reacting with potassium.

Notice also that the plots of ΔG against temperature for sodium and magnesium change direction.

This is due to the boiling points of the metals. Sodium's boiling point is 1156K (883°C). Above this temperature, Na is a gas and therefore has a high entropy value. The equation shown would therefore have 5 moles of gas turning into 1 mole of solid. ΔS would be large and negative, therefore $-T\Delta S$ would become more positive.

Practice questions

- 1) Determine the temperature at which the decomposition of ammonium chloride into ammonia and hydrogen chloride gases becomes feasible. The thermodynamic data values are:

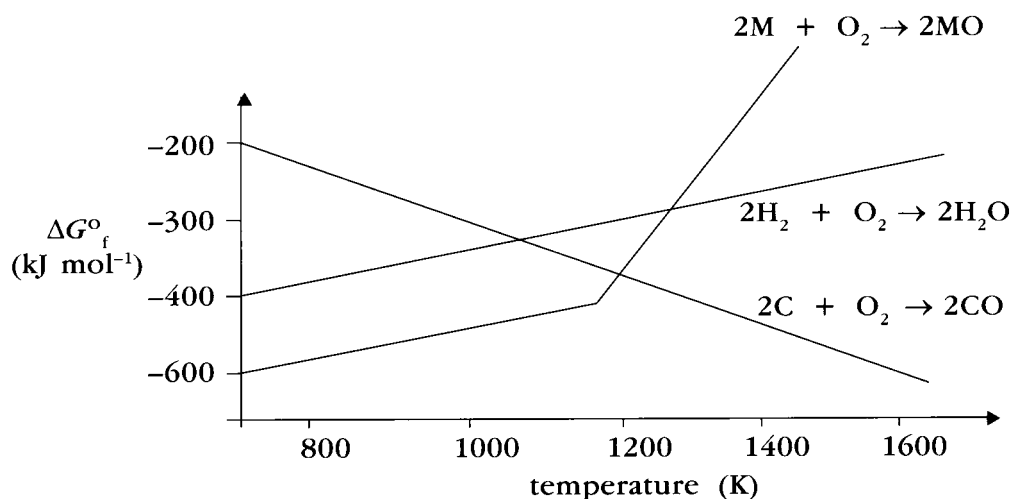
	ΔH_f° (kJ mol ⁻¹)	S° (J mol ⁻¹ K ⁻¹)
ammonium chloride	-314	96
ammonia	-46	193
hydrogen chloride	-92	187

- 2) Methane reacts with steam to produce synthesis gas
 $\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2$ reactants and products are all gases

- (a) Prove that this reaction is not feasible at 298K
 (b) Determine the temperature at which this reaction becomes feasible.
 The thermodynamic data values are:

	ΔH_f° (kJ mol ⁻¹)	S° (J mol ⁻¹ K ⁻¹)
CH ₄ (g)	-75	186
H ₂ O(g)	-242	189
CO(g)	-110.5	198
H ₂ (g)	0	131

- 3) The Ellingham diagram for the reduction of a metal M from its oxide MO is shown



What is the minimum temperature that metal M can be obtained from its oxide using

- (a) hydrogen
 (b) carbon

Chemical kinetics

Introduction

Chemical kinetics is the study of the speed of chemical reactions. From Int 2 and Higher you already know that the speed or rate of a chemical reaction depends on factors such as temperature, concentration of the reactants, particle size and whether a catalyst is present or not.

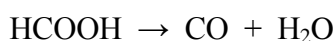
It is also known that all reactions have an activation energy and that an activated complex is formed.

In this section, we are now concerned with the development of these ideas on a more quantitative basis, in which mathematical models are used to state precisely how the concentration of reactants influences the speed of a chemical reaction.

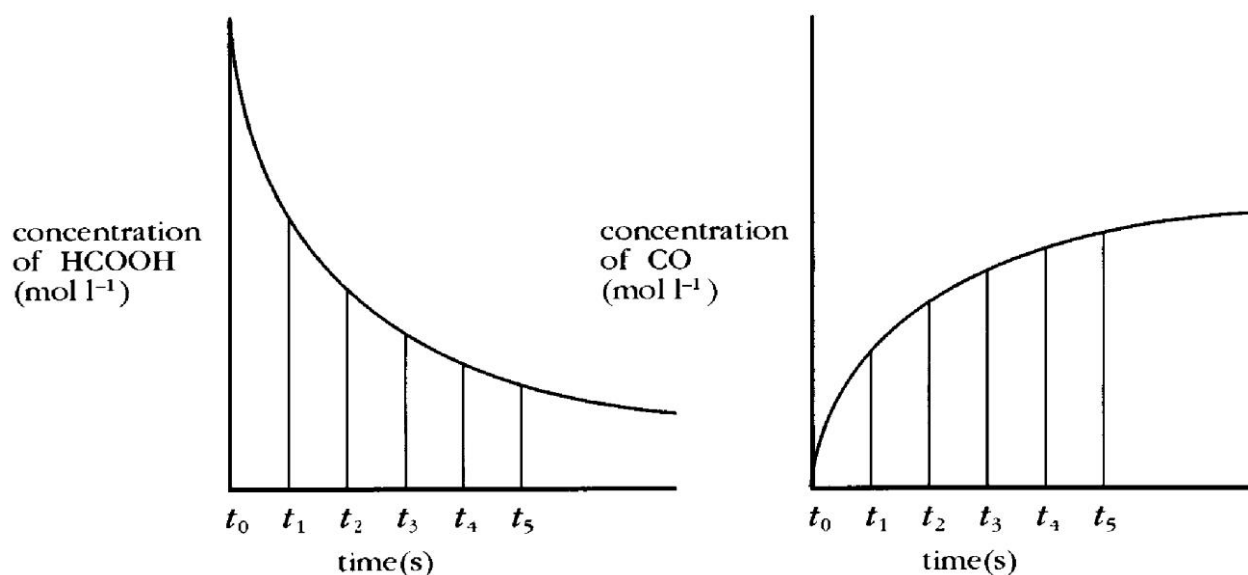
We are also interested in how such information can be used to gain an insight into the pathway by which the reaction takes place.

Reaction rate is expressed as a change in concentration of reactant or product in unit time.

Expressed in this way, the rate is independent of the size of the sample under consideration. For example, in the decomposition of methanoic acid



we can determine the reaction rate by following either the decrease in concentration of the acid or the increase in carbon monoxide concentration with time.



The average reaction rate is the change in concentration of either reactants or products divided by the time interval over which it is measured time. For example, over the time interval t₁ to t₂

$$\text{Rate} = -([\text{HCOOH}] \text{ at } t_2 - [\text{HCOOH}] \text{ at } t_1) \div (t_2 - t_1)$$

OR

$$\text{Rate} = ([\text{CO}] \text{ at } t_2 - [\text{CO}] \text{ at } t_1) \div (t_2 - t_1)$$

units measured in mol l⁻¹ (time)⁻¹
(time units are usually seconds)

You have already learned that concentration is expressed as the formula in square brackets.

Note that a negative sign must be used when dealing with rate of change of reactant as the calculation will always give a negative result.

The calculation shown will give an average rate over a time interval.

If we shorten the time interval to a very small value dt , the calculation will give us the instantaneous rate at time t . Mathematically, this translates into the use of differential calculus.

The rate equation becomes

$$\frac{-d[\text{HCOOH}]}{dt} \quad \text{or} \quad \frac{+d[\text{CO}]}{dt}$$

*It must be stressed at this point that **no** differential calculus will be involved in any calculations you require to do, but you should recognise that rate can be expressed using these units on a graph or in a table heading. Studies of kinetics at University level will involve calculus.*

The rate at any particular time t is given by the gradient of the tangent to the curve at time t . This will have a maximum value at time = 0 and it is therefore usual to determine initial rates of reaction and to use these values in the determination of other kinetic parameters.

Determining reaction rate by experiment

This is done by carrying out a reaction several times, each time varying the concentration of a reactant. The rate for one experiment is determined by measuring the concentration of a reactant or product at regular time intervals and then calculating reaction rate.

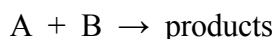
Concentration of reactant or product is found out by taking samples at regular time intervals and analysing.

For example, if an acid and alcohol are reacting to form an ester, small samples of the reaction mixture can be removed and the number of moles of acid determined by titration with an alkali.

If the reaction involves something like iodine, samples can be taken and titrated with sodium thiosulphate with starch as an indicator.

Once all the experiments have been carried out, the results are presented in a table.

If we consider a very simple reaction



We would carry out several experiments where we held $[\text{B}]$ constant and varied $[\text{A}]$ and then held $[\text{A}]$ constant and varied $[\text{B}]$.

Notice also that we only need to analyse for $[\text{A}]$, as rate is related to change in $[\text{A}]$. If $[\text{A}]$ changes, $[\text{B}]$ must also change according to the stoichiometry of the equation.

From the example described above, it is easy to analyse for an acid by titration, but more difficult to analyse for an alcohol. If 0.25 mol acid is used up in 10 minutes, 0.25 mol of alcohol must also be used up, and 0.25 mol of ester must be formed.

The results of a series of experiments might look like:

Expt.	[A] (mol l ⁻¹)	[B] (mol l ⁻¹)	Rate (mol l ⁻¹ s ⁻¹)
1	1.0	1.0	0.04
2	2.0	1.0	0.08
3	3.0	1.0	0.12
4	1.0	2.0	0.08
5	1.0	3.0	0.12

By comparing experiments 1,2 and 3, we can see that doubling [A] doubles the rate and tripling [A] triples the rate.

Meaning that the rate is directly proportional to [A].

By comparing experiments 1,4 and 5, we can see that doubling [B] doubles the rate and tripling [B] triples the rate.

Meaning that the rate is directly proportional to [B].

We can see that rate \propto [A], and that rate \propto [B]

We can derive the expression that rate \propto [A] [B] (doubling both [A] and [B] would increase the rate by a factor of 4).

Applying more mathematical theory, the rate = a constant X [A] [B]

Rate = k [A] [B],

where k = the **rate constant** for this particular reaction

Since reaction rates vary with temperature, it is obviously important that any set of kinetics experiments be carried out under identical conditions except variation of concentration of reactants.

Introducing powers and order

All chemical kinetics results are always related to **powers** of numbers, and the **order** of a chemical reaction is the sum of then powers of the reactants involved.

For the example above,

Rate = k [A] [B]

Applying powers, Rate = k [A]¹ [B]¹

The reaction is **first order** with respect to [A] and also first order with respect to [B]

The reaction is **second order** overall (sum of powers = 2)

Calculating the value of the rate constant

Rate = k [A] [B]

0.04 = k X 1.0 X 1.0

k = 0.04

Consider another example

Expt.	[A] (mol l ⁻¹)	[B] (mol l ⁻¹)	Rate (mol l ⁻¹ s ⁻¹)
1	1.0	1.0	0.04
2	2.0	1.0	0.08
3	3.0	1.0	0.12
4	1.0	2.0	0.04
5	1.0	3.0	0.04

From this we can see that the rate varies as [A], but changing [B] has no effect on the rate.

From your knowledge of mathematics, we need a power that, no matter what the number is, raising it to this power will always give the same answer. The power is zero. Any number raised to the power of zero will always give 1

The reaction is therefore first order with respect to [A], and **zero order** with respect to [B]

Rate = k [A]¹ [B]⁰, and the overall order is 1 + 0, = first order.

The general rate equation

If n molecules of A react with m molecules of B, in the absence of any other experimental data, the rate equation for the reaction would be:

$$\text{Rate} = k [\text{A}]^n [\text{B}]^m$$

So the general reaction $2\text{A} + \text{B} \rightarrow \text{products}$ would have the rate equation $\text{Rate} = k [\text{A}]^2 [\text{B}]^1$
It would be second order with respect to [A], first order with respect to [B], and be third order overall.

It is worthwhile to note at this point that it is only *whole number* powers are involved in kinetics. There is no reaction where rate = k [A]^{1/2} for example. This is due to the fact that only whole numbers of molecules can react.

What kinetic studies tell us about a reaction

It is believed that most chemical reactions proceed by one or more steps. Simple reactions are usually only one or two steps, whereas more complex reactions may take more than this.

Consider the burning of propane in air in a gas burner

The equation is $\text{C}_3\text{H}_8 + 5\text{O}_2 \rightarrow 3\text{CO}_2 + 4\text{H}_2\text{O}$

For this reaction to proceed in one step would involve the simultaneous collision of one propane molecule with five oxygen molecules. This is very unlikely given that gas molecules are widely spaced and only one in five molecules in air is oxygen. There must be some intermediate steps. What the intermediates actually are is anybody's guess as the reaction proceeds too fast to even attempt a determination.

If we look at a simpler reaction, we can start to build up an idea.

Consider hydrogen peroxide reacting with hydrogen iodide

The equation is $\text{H}_2\text{O}_2 + 2\text{HI} \rightarrow 2\text{H}_2\text{O} + \text{I}_2$

The rate law would predict the kinetics to be $\text{Rate} = k [\text{H}_2\text{O}_2] [\text{HI}]^2$

In actual fact, the experimentally observed rate law is $\text{Rate} = k [\text{H}_2\text{O}_2] [\text{HI}]$

This suggests that the reaction takes place in two steps

Step 1 $\text{H}_2\text{O}_2 + \text{HI} \rightarrow \text{intermediate}$ (a very slow step)

Step 2 $\text{intermediate} + \text{HI} \rightarrow 2\text{H}_2\text{O} + \text{I}_2$ (a very fast step)

The reasoning behind this is that if a chemical reaction proceeds in two or more steps, **the rate is determined by the slowest step**, no matter where in the reaction this step occurs.

The slowest step is called the **rate determining step (r. d. s.)**.

Since the number of molecules in the reaction above is small, there are only a small number of possible intermediates. Other analysis methods such as isotopic labelling used in conjunction with kinetic studies have produced the following reaction mechanism.

You are not expected to know about isotopic labelling at Advanced Higher, but you will likely come across it at University. It is not difficult to make molecules with the heavier isotopes of hydrogen or oxygen and identify these isotopes in the products formed.

Step 1 $\text{H}_2\text{O}_2 + \text{HI} \rightarrow \text{H}_2\text{O} + \text{HOI}$ slow (r. d. s.)

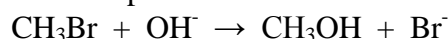
Step 2 $\text{HOI} + \text{HI} \rightarrow \text{H}_2\text{O} + \text{I}_2$ fast

So the overall rate depends on the collisions between one H_2O_2 molecule and one HI molecule.

Reactions of halogenoalkanes with hydroxide ions (alkaline hydrolysis)

Reaction 1

If bromomethane (a primary halogenoalkane) is reacted with sodium hydroxide solution, the OH^- ions replace the Br atom and produce the alcohol + a Br^- ion.



Kinetic studies show that $\text{rate} = k [\text{CH}_3\text{Br}] [\text{OH}^-]$

This suggests that the reaction takes place in one step, with the intermediate being an unstable particle containing both a Br and an OH group. The rate at which this is formed depends on the rate of collisions between the two reactants.

The C-OH bond is partially formed and the C-Br bond is partially broken.

Reaction 2

If 2-bromo-2-methylpropane - $(\text{CH}_3)_3\text{CBr}$ - is reacted in the same way, kinetic studies show that

$\text{Rate} = k [(\text{CH}_3)_3\text{CBr}]$

This suggests a two-step reaction, with the intermediate being formed from only the $(\text{CH}_3)_3\text{CBr}$ in a slow step.

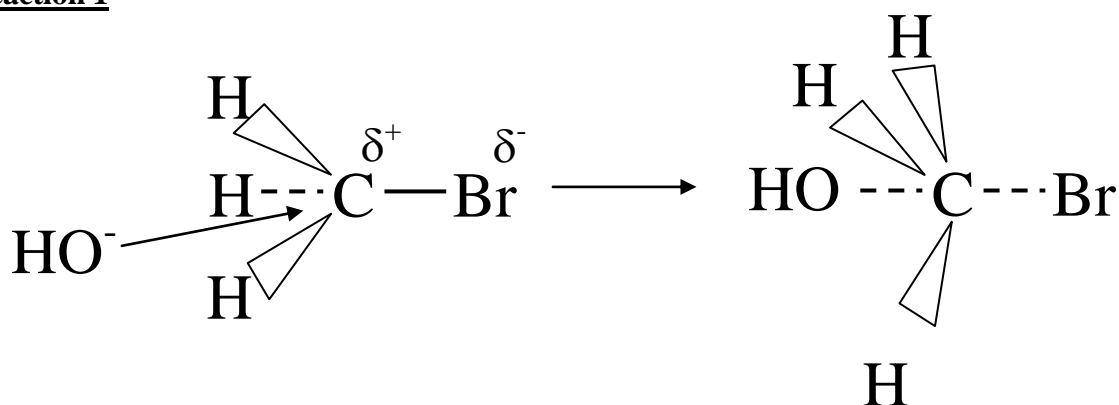
Step 1 - $(\text{CH}_3)_3\text{CBr} \rightarrow (\text{CH}_3)_3\text{C}^+ + \text{Br}^-$ (slow step) (C-Br bond breaking fully is not likely to happen easily)

Step 2 - $\text{C}_4\text{H}_9^+ + \text{OH}^- \rightarrow \text{C}_4\text{H}_9\text{OH}$ (fast step)

The $[\text{OH}^-]$ does not matter as they cannot enter the reaction until C_4H_9^+ has been formed.

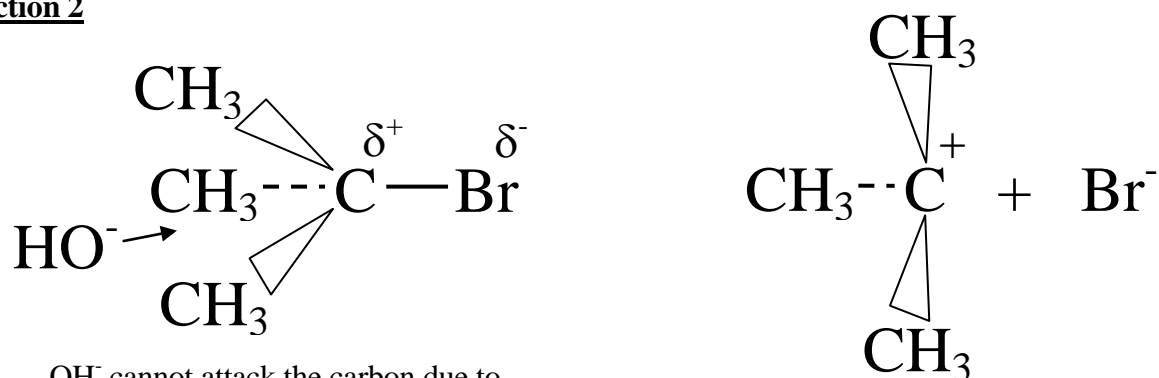
Diagrams of the suggested reaction mechanism

Reaction 1



The intermediate then goes on to form the alcohol and a bromide ion

Reaction 2



OH^- cannot attack the carbon due to the bulky methyl groups blocking its path.

In organic chemistry this is known as the steric effect or steric hindrance.

Not needed for Advanced higher but will make its appearance in University organic chemistry.

This intermediate is not easily formed, so the step is slow and does not depend on the presence of OH^- .

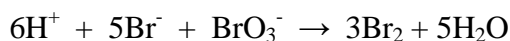
Once the positive ion is formed, it is rapidly attacked by OH^- forming the alcohol.

This step could be millions of times faster than the first.

Note that we cannot establish the exact mechanism of a reaction with absolute certainty. We can only suggest a *possible* mechanism that is consistent with the kinetics.

Practice questions

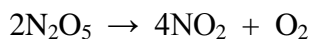
- 1) Bromide ions and bromate ions react in acid solution according to the equation



Rate measurements on four different reaction mixtures gave the following data.

Mixture	$[\text{H}^+]$	$[\text{Br}^-]$	$[\text{BrO}_3^-]$	Relative rate
1	0.45	0.375	0.075	1
2	0.45	0.75	0.075	2
3	0.9	0.375	0.075	4
4	0.45	0.375	0.15	4

- (a) What is the rate expression for the reaction?
(b) What is the order of the reaction with respect to each of the reactants?
(c) What is the overall order of the reaction?
(d) Explain why the rate equation and the overall equation are different.
- 2) Dinitrogen pentoxide decomposes according to the equation



The reaction rates for the above reaction at various starting concentrations are given in the table.

$[\text{N}_2\text{O}_5](\text{mol l}^{-1})$	Rate ($\text{mol l}^{-1} \text{s}^{-1}$)
2.20	2.25×10^{-5}
2.00	2.10×10^{-5}
1.52	1.58×10^{-5}
0.95	0.96×10^{-5}

- (a) Draw a graph of the rate against $[\text{N}_2\text{O}_5]$.
(b) Calculate the value of the rate constant.